INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology **16** (2005) S59–S62 doi:10.1088/0957-4484/16/3/011

Hysteretic behaviour of the tip–sample interaction on an InAs(110) surface: an *ab initio* study

V Caciuc[1], H Hölscher[1,2], S Blügel[3] and H Fuchs[1,2]

[1] Physikalisches Institut, Westfälische Wilhelms Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany
[2] Center for Nanotechnology (CeNTech), Gievenbecker Weg 11, 48149 Münster, Germany
[3] Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

Received 5 October 2004, in final form 18 November 2004
Published 14 January 2005
Online at stacks.iop.org/Nano/16/S59

Abstract
We performed an *ab initio* study of tip–sample interactions between an SiH_3 tip and an InAs(110) surface when the tip is on top of As and In atoms. The calculated force curves and the corresponding normalized frequency shift curves exhibit discontinuities. We analysed these jumps in the force curves from the point of view of the structural changes of the InAs(110) surface due to its interaction with the tip and compared them with those obtained for an Si(111) 7×7 surface. The simulation of a complete NC-AFM image shows reasonable agreement with the experiment.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

With the advent of *atomic force microscopy* (AFM) [1] it became possible to obtain resolution at the atomic scale for insulator, semiconductor and conductive surfaces [2–4]. At variance with *scanning tunnelling microscopy* (STM), this method can also be used for imaging non-conductive surfaces. However, the 'true' atomic resolution (i.e., the observation of single atomic-scale point defects) could be achieved so far only in ultra-high vacuum (UHV). In this context, one of the most frequently used detection schemes is the *frequency modulation* proposed by Albrecht *et al* [5], which relies on the dynamics of a self-driven oscillator. A schematic illustration of the experimental set-up used in *non-contact atomic force microscopy* (NC-AFM) is shown in figure 1(a).

A common feature of STM and AFM is represented by the fact that the recorded images are *topological*, which implies that there is no one-to-one correspondence between the features of the experimental AFM (STM) pictures and the atomic positions on the corresponding surfaces. Therefore, only atomistic simulations can provide the understanding of the physical origin of the observed atomic scale contrast of the experimental AFM images. Such calculations performed for semiconductor surfaces [6–11] and ionic ones [12–16] clearly emphasized the crucial role of short-range chemical

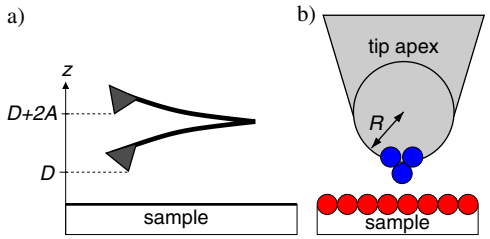

Figure 1. (a) In non-contact atomic force microscopy a cantilever with an integrated tip is vibrated with oscillation amplitude A close to the sample surface. The resonance frequency of the oscillating cantilever changes due to the interaction between the tip and the sample surface. During the imaging process the tip–sample distance of closest approach D is varied such that a map of *constant* frequency shift is recorded. (b) The tip–sample interaction is divided into short- and long-range forces. The long-range part is described by the van der Waals force of a spherical tip with radius R. The short-range forces between the foremost tip atoms and the surface are modelled by *ab initio* calculations where the tip is represented by a small atomic cluster.

(electrostatic) tip–sample interactions in the mechanism of atomic-scale contrast.

Besides providing a fundamental understanding of the microscopic origin of the atomic-scale contrast observed in NC-AFM, *ab initio* simulations give an unique insight into the

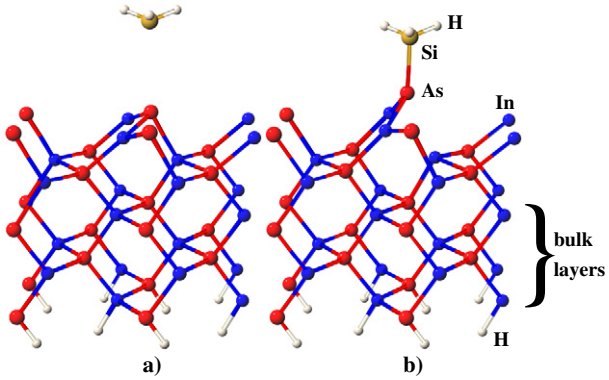

Figure 2. Ball-and-stick model of the atomic structure of an InAs(110) surface and an SiH_3 tip on top of As atom. (a) For a tip–sample distance of ≈4.4 Å the relaxation of the surface due to its interaction with the tip is negligible. (b) As the tip approaches the surface, at ≈3.6 Å the As atom is pulled out by the tip due to a breaking of one As–In bond while a chemical bond with the Si atom is formed.

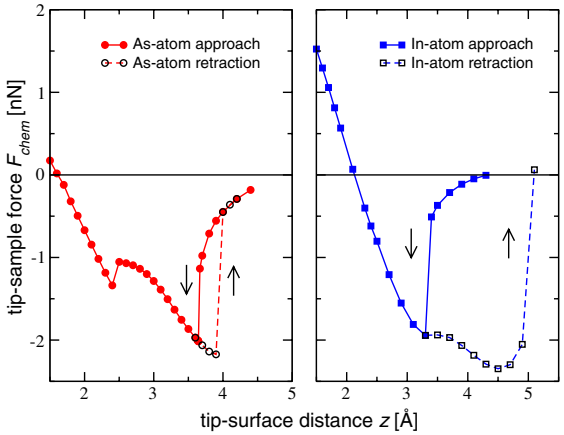

Figure 3. Short-range tip–surface interaction forces for an SiH_3 tip on top of As (left) and In (right) atoms.

atomic dynamics of the surfaces and AFM tips, information which is not available from experiment. The specific details of the atomic rearrangement induced by the tip–sample surface interaction have been speculated to be the origin of the discontinuities present sometimes in the frequency shift curves recorded for the Si(111) 7 × 7 surface [17–19]. In the present paper we report a similar behaviour for the InAs(110) surface as revealed by our *ab initio* calculations.

2. Method

As schematically depicted in figure 1(b), the AFM tip is assumed to consist of a microscopic cluster attached to a macroscopic body. The microscopic tip is used in *ab initio* simulations to evaluate the short-range chemical force while the long-ranged ones (usually, van der Waals forces) are taken into account by the macroscopic part of the tip. Since the experimental NC-AFM investigation of the InAs(110) surface performed by Schwarz *et al* [20, 21] was carried out with clean sputtered silicon tips, we assumed tips of the same material in our simulations. The microscopic part of the tip is modelled by an SiH_3 molecule with three dangling bonds saturated by three H atoms and one dangling bond pointing toward the surface as already used in the literature [22, 23].

First-principles total-energy calculations for the InAs(110) surface were carried out using the pseudopotential method [24] as implemented in our fully parallelized EStCoMPP code [25]. The pseudopotentials used to describe the electron–ion interaction were generated according to scheme proposed by Bachelet *et al* [26] in the separable form of Kleinman and Bylander [27]. The local density approximation (LDA) [28] for the exchange-correlation energy functional was employed.

The InAs(110)(1 × 1) surface was modelled by a periodic slab consisting of five layers of In and As atoms separated by a vacuum region of ≈15.5 Å. The dangling bonds of the bottom surface were saturated by using a fractional charged hydrogen layer. In three atomic layers (including the bottom surface) the atomic positions were kept fixed to their bulk positions, while the atoms from the two surface layers were allowed to relax (see figure 2). The tip itself is monatomic and cannot be relaxed.

Convergent tip–surface interaction forces were obtained by expanding the Kohn–Sham wavefunctions over a plane-wave basis set with a kinetic energy up to E_{cut} of 9.0 Ryd. The Brillouin zone integrations were performed over 16 **k**-points in the irreducible part of the Brillouin zone using the method described by Monkhorst and Pack [29].

3. Simulation results

As briefly discussed in introduction, the atomic contrast in NC-AFM is essentially determined by the short-range chemical interaction between the tip apex atom and the surface. This implies that the tip–surface distance of closest approach D (see figure 1(a)) is comparable with the typical values of the lattice parameters in solids (i.e., some angstroms). In consequence, the short-range tip–surface interaction might be strong enough to induce a significant relaxation of the surface. Exactly this effect can be observed in our calculations.

The force curves as a function of the tip height z calculated for the SiH_3 tip on top of As and In atoms are shown in figure 3. A striking feature displayed by these force curves is the presence of a discontinuity when the tip approaches the surface on top of the As atom (at ≈3.7 Å) as well as when it is above the In one (at ≈3.2 Å). The exact values, however, might change by using larger tips, because the relaxation of the tip itself will change the tip–sample interaction (see, e.g., [9, 16]). An additional feature of the calculated force curves is that they exhibit a hysteresis for *both* atoms. The corresponding energy dissipation is ≈0.25 eV for the tip on top of the As atom and ≈2.1 eV when the tip is above the In one. This large difference for the energy dissipation between the two atomic sites is determined by different geometric positions of the As and In atoms (due to the surface relaxation in the absence of the tip, the In atom is 0.76 Å deeper than the As one).

A quite similar behaviour was reported by Ke *et al* for a silicon tip on top of a Ga atom for the GaAs(110) surface [8]. It was pointed out that this peculiar feature of tip–surface force curves is related to the presence of two local energy minima for the tip–sample interaction in a direction perpendicular to the surface (see also [2, p 291]).

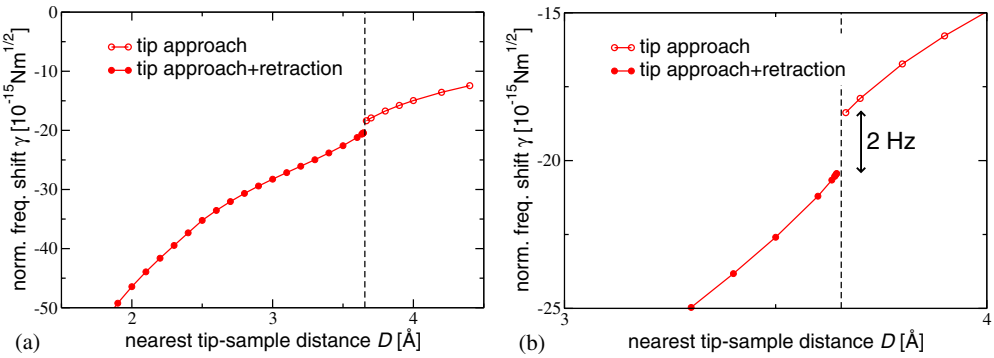

Figure 4. (a) Normalized frequency shift versus tip height curves calculated for the tip on top of an As atom. (b) A magnification of (a). A discontinuity in the frequency shift curve appears at ≈3.7 Å with a height of 2 Hz. Besides the calculated short-range chemical tip–sample interaction force, the long-range van der Waals forces have also been considered. The macroscopic part of the tip was assumed to be a sphere with a radius of 100 Å and a Hamaker constant of 0.1865 aJ.

A direct consequence of such hysteric behaviour is that the tip–sample interaction is no longer conservative, i.e., there are discontinuous structural changes of the sample surface which lead to an energy dissipation (see, e.g., chapters 15, 19 and 20 in [2] and [4, 30]). Besides the energy dissipation due to non-conservative tip–sample interaction, sometimes discontinuities in frequency shift versus tip height curves have been observed. More specifically, the NC-AFM investigation of Si(111) 7 × 7 performed by Uchihashi *et al* [17] revealed that, after accidental contact between the silicon tip and the surface, frequency shift curves displaying a discontinuity at certain tip–surface distance as well as curves without such a discontinuity have been observed. It is important to note that, this sudden jump in the frequency shift was *not* determined by the crash of the AFM tip into the surface during recording that frequency shift curve. A similar behaviour for the same Si(111) 7 × 7 surface was observed by Morita *et al* [18]. Moreover, they reported that the discontinuous frequency shift curves are *site* dependent, being associated with a strong attractive tip–sample interaction due to a sudden formation of a chemical bonding between the tip apex atom and silicon surface adatom when the tip moves towards the surface. Similar jumps in the frequency shift versus tip–surface distance curves have been observed by Oyabu *et al* [19] in the context of atomic manipulation by soft nanoindentation on the same silicon surface.

The basic assumption that the discontinuities present in the frequency shift curves in the absence of the tip–surface crashes are related to the onset of a strong covalent bonding between the AFM tip and the sample surface is supported by our *ab initio* results obtained for the InAs(110) surface. As described in [31], the frequency shift measured in a system where dissipative tip–surface forces are also present depends only on the average of the tip–sample interaction force between the forward $F_{\downarrow}$ and backward $F_{\uparrow}$ forces:

$$\Delta f \cong -\frac{f_0}{\pi A^2 c_z}\int_{-A}^{A}\frac{F_{\downarrow}+F_{\uparrow}}{2}\frac{z}{\sqrt{A^2-z^2}}\,\mathrm{d}z \qquad (1)$$

where, briefly, A represents the oscillation amplitude, and f_0, c_z and z stand for the mechanical eigenfrequency, spring constant and position of the cantilever, respectively.

As is clearly shown in figure 3, the tip–surface interactions for the SiH_3 tip on top of As and In atoms exhibit different characteristics when the tip approaches the surface and when it moves away from it. This implies that one can identify $F_{\downarrow}$ from equation (1) with the calculated short-range forces when the AFM tip moves towards the surface and $F_{\uparrow}$ with those obtained when the tip is retracted from it. Focusing on the case of the tip above As atoms, it is now important to observe that the tip can be retracted without hysteresis if it comes no closer than 3.7 Å to the sample surface. If the tip is beyond this discontinuity in the force curve, there is a hysteresis. Consequently, the calculated frequency shift curve also presents a discontinuity as in the corresponding force curve. Figure 4 displays the normalized frequency shift $\gamma(D) = (c_z A^{3/2}/f_0)\Delta f(D)$ [32].

As can be seen from figure 2, the origin of the discontinuity in the force curve when the tip approaches the surface is the onset of a strong covalent bonding between the dangling bond of the tip apex atom and that of the As one, while one As–In chemical bond is broken. More specifically, the As atom jumps in the normal direction towards the tip when the tip–sample distance is ≈3.7 Å with a jump height of ≈0.7 Å.

This scenario was assumed to take place for the tip–sample interactions on Si(111) 7 × 7. Our *ab initio* simulations performed for the InAs(110) surface strongly suggest that such a mechanism indeed involves sudden changes of the surface structure due to its strong chemical interaction with the AFM tip. Such a situation should occur whenever an AFM tip with dangling bonds comes sufficiently close to a reactive surface. However, one should keep in mind that thermal fluctuations might lead to a 'smoothing' of this discontinuity. Furthermore, the experimental results were obtained in the so-called *constant-excitation* [33] mode which is slightly different from the original method introduced by Albrecht *et al* [5]. As observed by the simulations of Gotsmann and Fuchs [34, 35] for this specific mode, the oscillation amplitude might switch between two states in such a way that the hysteresis takes places only for a fraction of oscillation cycles. Due to this behaviour the frequency shift curve does not show a discontinuity but a continuous linear decay which might be observed as a step in the experiment.

Since the tip–sample forces show no hysteresis before the discontinuity, we assumed that the surface relaxation due to the tip–sample interaction does not *qualitatively* change the frequency shift maps obtained on the basis of short-range

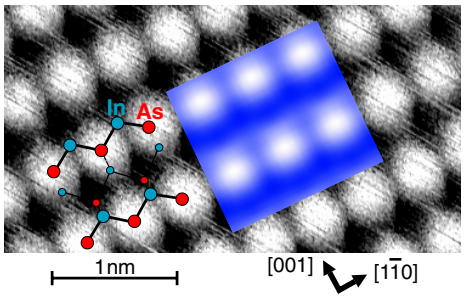

Figure 5. Comparison between the experimental and simulated NC-AFM image of InAs(110) for a silicon tip. Due to the simulation the maxima observed in the experiment can be unambiguously assigned to As atoms.

chemical forces. Therefore, we simulated NC-AFM maps of constant frequency shift by ignoring the surface relaxation due to its interaction with the tip. In figure 5 (inset) we present a simulated NC-AFM image which was calculated with the assumption that the tip is always well before the instability (for details see [36]).

The basic feature of the simulated image is that only the As sublattice is imaged, as can be seen by a comparison with the surface structure of InAs(110) displayed on the left-hand side. Furthermore, it can be observed that the position of the In atom does not appear as a specific feature in the simulated NC-AFM image. This outcome of our simulations does not change with the parameters assumed for the macroscopic part of the tip (radius, Hamaker constant and offset between microscopic and macroscopic part of the tip). Our simulated image is in agreement with the experimental ones obtained by Schwarz *et al* [20]. Their analysis revealed that when using clean silicon tips the recorded NC-AFM images consisted of rows of bright protrusions which were assigned to the As atom on the basis of a pure geometrical analysis. This conclusion is fully confirmed by our calculations.

4. Conclusion

Our *ab initio* simulations carried out for vertical scans of an SiH_3 tip above As and In atoms of an InAs(110) surface revealed the presence of discontinuities in the force curves as a function of the tip–surface distance. This feature was observed for the case when the tip approached or moved away from the surface. The normalized frequency shift calculated for the tip on top of an As atom when it moves towards the surface also displayed a discontinuity at the tip–sample distance where a sudden strong covalent bond between the As atom and Si tip apex atom is formed. This theoretical finding for the InAs(110) surface is comparable with the experimental observation of similar discontinuities in frequency shift curves recorded for silicon tips interacting with the Si(111) 7×7 surface. The simulation of a complete NC-AFM image shows reasonable agreement with the experiment.

Acknowledgments

The authors acknowledge fruitful discussions with A Schwarz (University of Hamburg) and A Schirmeisen (University of Münster). This work was supported in part by the DFG (Grants No. BL 444/2-1 and HO 2237/2-1), the BMBF (Grant No. 03N8704) and the 'Ministerium Wissenschaft und Forschung des Landes Nordhein-Westfalen'. The computational grant 'Rasterkraftmikroskopie' from Forschungszentrum Jülich is gratefully acknowledged.

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